Complexes of Divalent Tellurium with Thiourea

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Square planar complexes of divalent tellurium with thiourea have been studied in this laboratory since 1959 [1]. Of the type $Te(tu)_2X_2$ where tu = thiourea, they include those with X = chloride [1], bromide [1], iodide, thiocyanate [1], and methanethiosulphonate [2]. Crystal structure determinations of the chloride [3], bromide [4] and methanethiosulphonate [5] have been carried out, and a Fourier analysis of one zone of the thiocyanate [6]. The crystals of the three halides are isomorphous; of the two possible isomers, *cis* and *trans*, of a square planar complex of this type, they represent the *cis* isomer, as does also the thiocyanate, while the methanethiosulphonate is *trans*. Of the same type and also *trans*, are two salts [7], the chloride and bromide, of a divalent tellurium cation with two thiourea and two tetramethylthiourea ligands; the two salts are isomorphous and crystallize in the space group $C_{2h}^5-P2_1/c$ with two molecules per unit cell so that the cations are centrosymmetric.

Vřešťál [8] has independently prepared the chloride and bromide, $Te(tu)_2Cl_2$ and $Te(tu)_2Br_2$, and Němec [9] has determined the unit cells and space group. Their results agree with ours [1].* The purpose of this note is to describe the iodide, and to give preparative and analytical data for the thiocyanate [1]. Salts of the cation $Te(tu)_4^{2+}$ form the subject of a following note [10].

Diiodo-dithiourea-tellurium(II), $Te(tu)_2I_2$, crystallizes from aqueous thiourea solutions of a tetrathiourea-tellurium(II) salt such as the chloride or bromide (or of $Te(tu)_2Cl_2$ or $Te(tu)_2Br_2$ which dissolve in aqueous thiourea to give these salts) and potassium iodide: 6 g of $Te(tu)_2Br_2$ was dissolved in 200 ml of 10 % aqueous thiourea at 35°, traces of tellurium were filtered off, and 10 g of potassium iodide in 50 ml of water was added. After 24 h at room temperature the brownish red crystals of $Te(tu)_2I_2$ were filtered off, and washed with ethanol containing a little thiourea, and then with ether. Yield, 4.9 g (67 %). (Found: S 10.53; Te 25.28. Calc. for $C_2H_8I_2N_4S_2Te$: S 12.02; Te 23.91.) The analytical results indicate that the samples were not quite pure, or that there is a little less than two thiourea units in the molecule. The samples on microscopic inspection appeared homogeneous, and the crystals were found to be isomorphous with those of the chloride and bromide, for which the analytical data are quite satisfactory.

The crystals occur as prisms extended along the *b* axis, or as plates {100}. The unit cell dimensions are listed below, together with, for comparison, those of the chloride and bromide [1].

	a	*b*	*c*	*β*
$Te(tu)_2Cl_2$	9.90 Å	7.62 Å	14.10 Å	100 ½°
$Te(tu)_2Br_2$	10.10	7.74	14.67	100°
$Te(tu)_2I_2$	10.24	7.93	15.59	100°

The space group is C_{2h}^6-I2/c, and there are four molecules per unit cell; the tellurium atoms lie on twofold axes of symmetry.

Dithiocyanato-dithiourea-tellurium(II), $Te(tu)_2(SCN)_2$, was prepared from the chloride or bromide, and ammonium thiocyanate: To a solution of 165 g of ammonium thiocyanate in 150 ml of water, at 70–80°, was added 5 g of $Te(tu)_2Br_2$ under stirring. A red solution resulted which deposited a little tellurium; after filtering, the solution was placed in a refrigerator over night. The crystals were then filtered off, and washed with ethanol containing a little concentrated hydrochloric acid, and then with ether. Yield, 2.7 g (60 %). (Found: S 32.18; Te 32.19. Calc. for $C_4H_8N_6S_4Te$: S 32.29; Te 32.22.) Similar results were obtained by use of the chloride instead of the bromide. Unit cell and space group data have been reported earlier [1]. As mentioned [1], the compound was obtained as prisms when prepared from the chloride and as plates from the bromide. The plates rapidly grew into prisms when brought in contact with aqueons or dilute ethanolic hydrochloric acid.

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* Minor divergencies are: Vřešťál [8] gives m.p. 184° (decomp.) for the chloride, $Te(tu)_2Cl_2$; we found 220° (decomp.). Vřešťál [8] obtained two forms of the bromide, $Te(tu)_2Br_2$, which gave "practically identical" X-ray powder photographs: Plates (from dilute solutions) with m. p. 170° (decomp.) and density 2.57 g/cm³, and short prisms (from more concentrated solutions) with m. p. 220° (decomp.) and density 2.47 g/cm³; we found m. p. 220° (decomp.) and density 2.58 g/cm³ (X-ray density calc. 2.59 g/cm³). We have not been able to identify more than one crystalline form of any $Te(tu)_2X_2$ complex.

The TeS$_2$Cl$_2$ and TeS$_2$Br$_2$ groups in Te(tu)$_2$Cl$_2$ and Te(tu)$_2$Br$_2$ have, according to two-dimensional crystal structure analyses, the dimensions: Te–S = 2.48 Å, Te–Cl = 2.92 Å, ∠S–Te–S = 93°, ∠ Cl–Te–Cl = 93° in the chloride[3]; Te–S = 2.47 Å, Te–Br = 3.05 Å, ∠S–Te–S = 95°, ∠Br–Te–Br = 93° in the bromide[4]. The groups are almost but not exactly planar, the Te–Cl bonds being rotated 8° and the Te–Br bonds 9° out of the S–Te–S plane, to opposite sides of the plane in accordance with the twofold axis of molecular symmetry.

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Tetrathiourea-tellurium(II) Salts

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The salts Te(tu)$_4$Cl$_2$·2H$_2$O and Te(tu)$_2$Br$_4$ (tu = thiourea) were described and unit cell and space group data reported in 1959[1]. The chloride dihydrate crystallizes in the space group $C_{2h}^5-P2_1/c$ with two formula units per unit cell, which shows that the tellurium atom lies in a centre of symmetry and the TeS$_4$ group of the complex is thus planar. A two-dimensional structure analysis has subsequently been carried out[2]; the Te–S bonds are 2.69 Å and the S–Te–S angles 90°.

Some other salts have later been prepared and characterized, namely an anhydrous chloride, a thiocyanate, nitrate and perchlorate. Vřešťál[3] has independently prepared several tetrathiourea-tellurium(II) salts, and Němec[4] has studied the morphology and unit cells of the chloride dihydrate and perchlorate. Our results are reported below to the extent that they do not duplicate Vřešťál's and Němec's data.

Unit cell dimensions were derived from oscillation and Weissenberg photographs, using Cu$K\alpha$ radiation, λ = 1.542 Å. Axial lengths are believed to be accurate to within 0.5 %. Densities were determined by flotation in carbon tetrachloride-bromoform mixtures.

The salts are yellow, and stable in the solid state, but become black in contact with water, due to hydrolysis and subsequent dismutation into zero- and tetravalent tellurium. They hydrolyze slightly in contact with 96 % ethanol, and were on the preparative filters in most cases washed with 96 % ethanol containing a little thiourea or concentrated hydrochloric acid, and then with ether. Solutions in aqueous or ethanolic thiourea are fairly stable. The salts dissolve readily in dimethylformamide, to give orange-yellow to orange solutions, apparently stable at room temperature.

Tetrathiourea-tellurium(II) dichloride dihydrate, Te(tu)$_4$Cl$_2$·2H$_2$O. As reported[1], and confirmed through structure analysis[2], this salt is monoclinic. Němec[4], from morphological study and rotation photographs about three axes, described it as triclinic, obviously because his a and b axes, the rotation photographs about which[4] "are quite identical, referring not only to the length of axes, but also to the distribution of diffraction spots and their intensities", were not recognized as bc diagonals in space group $P2_1/c$.

The salt can be prepared by mixing, at about 80°, a solution of 2.4 g (15 mmoles) of tellurium dioxide in 10 ml of concentrated hydrochloric acid and 10 ml of water, and a solution of 7.5 g (99 mmoles, 10 % excess) of thiourea in 50 ml of water. The mixture is allowed to cool to about 30° and the crystals then filtered off. Yield, 7.9 g (98 %). The mother liquor on further cooling deposits crystals of formamidinium disulphide dichloride. Vřešťál[3] used more dilute solutions. The salt was also prepared as follows: 5.6 g of Te(tu)$_2$Cl$_2$ was dissolved, under stirring and warming to 40–50°, in a solution of 24 g of thiourea in 160 ml of 48 % ethanol. Some undissolved matter and a little tellurium was filtered off, and the filtrate allowed to stand at room temperature over night. Yield, 5.5 g (64 %). Analytical data for this salt, and for the